[illegible]
O. S. U. LIBRARY

UNITED STATES
DEPARTMENT OF THE INTERIOR
HAROLD L. ICKES, SECRETARY

BUREAU OF MINES
R. R. SAYERS, DIRECTOR

INFORMATION CIRCULAR

HYDROGEN SULFIDE POISONING AS A HAZARD IN THE PRODUCTION OF OIL

BY

SARA J. DAVENPORT

I.C. 7329,
July 1945.

INFORMATION CIRCULAR

UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

HYDROGEN SULFIDE POISONING AS A HAZARD IN THE PRODUCTION OF OIL[1]

By Sara J. Davenport[2]

CONTENTS

	Page
Introduction	1
Properties of hydrogen sulfide	2
Toxicity of hydrogen sulfide	2
Physiological action of hydrogen sulfide.	4
Treatment of hydrogen sulfide poisoning.	5
Prevention of hydrogen sulfide poisoning.	6
Precautions	6
Protective equipment	7
Detection of hydrogen sulfide in air	8
Bibliography	9

INTRODUCTION

Hydrogen sulfide has been listed (1)[3] as a possible hazard in 50 occupations, many of which are in the mineral industries. The effects of its occurrence in the petroleum industry made themselves felt more than two decades ago, resulting in a comprehensive study (2) of the toxic gases from Mexican and other high-sulfur petroleum products. The mining industry, likewise, has had cause to guard against this gas. Enough hydrogen sulfide has been found in coal and some noncoal mines during normal operations to cause severe eye irritation, some serious illness, and even fatalities. It is usually a product of the decomposition of sulfur compounds and may be produced by burning explosives containing sulfur; the gas in harmful quantities is formed by the use of black blasting powder or by the use of dynamite in blasting sulfide ores. Hydrogen sulfide is readily soluble in water, and enough may be released from water streams in coal and noncoal mining to cause fatal poisoning; it is found sometimes in stagnant water underground, particularly where ventilation currents are absent, and great care must be exercised when accumulations of such waters are disturbed, as exposure to comparatively low concentrations of the gas evolved therefrom has caused fatal accidents.

---

[1] The Bureau of Mines will welcome reprinting of this paper provided the following footnote acknowledgment is used: "Reprinted from Bureau of Mines Information Circular 7329."

[2] Information specialist (translator), Bureau of Mines.

[3] Numbers in parentheses refer to bibliography at end of this circular.

In 1942, four men who were attempting to seal off water that was entering a shaft, preparatory to resuming mining, were affected by hydrogen sulfide to the extent that two of them lost 1 day's work, a third 2 days' work, and the eyes of the fourth were affected, although he was able to remain at work. The hydrogen sulfide detector showed 0.0025 percent hydrogen sulfide 6 feet above the water with the fan running and 0.04 percent 3 feet above the water after the fan was stopped for 5 minutes. Investigation of such accidents has revealed that apparently hydrogen sulfide gas is more toxic in humid air such as is present in many mines. A still greater hazard is drilling into a pocket of methane and hydrogen sulfide, which is not a rarity and may be attended by fatal results (3).

The number of oil fields in the United States that produce "sour" crude oils containing hydrogen sulfide and other sulfur compounds has increased in recent years. The gas present in these fields, and that which escapes from tanks in which the crude oil is stored, or evolves during some of the refining processes, is lethal in the higher concentrations of hydrogen sulfide. Several deaths have resulted from carelessness and failure to take proper precautions to avoid exposure (4). Increased activity in oil fields producing sour crude oils with the possibility of exposure of the employees to a poisoning hazard has prompted the Bureau of Mines to call attention again to the toxicity of hydrogen sulfide.

PROPERTIES OF HYDROGEN SULFIDE

Hydrogen sulfide is a colorless, inflammable gas having an offensive odor and a sweetish taste. Its specific gravity is 1.1895, molecular weight 34.20, melting point -83.8° C., and boiling point -60.2° C., (5). The limits of inflammability are low 4.3 and high 45.5 (6). A mixture of two volumes of hydrogen sulfide with three volumes of oxygen explodes violently when ignited. Hydrogen sulfide is soluble in water at ordinary temperatures, one volume of water absorbing about three times its own volume of the gas (7). It is soluble in hydrocarbons such as gasoline, kerosine, and crude oil.

The offensive odor, like that of rotten eggs, is not reliable as a warning indication of its presence in dangerous concentrations, as persons differ greatly in the ability to detect smells, and furthermore the sense of smell tires readily and is of little value thereafter in noting even greatly increased concentrations; high concentrations have a rapidly paralyzant effect on the olfactory nerve.

TOXICITY OF HYDROGEN SULFIDE

Hydrogen sulfide is an irritant and extremely toxic gas; in fact, it is almost as toxic as hydrogen cyanide and five or six times as toxic as carbon monoxide. Although employees in oil fields where hydrogen sulfide is present may become so habituated to the smell of the gas as not to notice it, tolerance of its effects is not acquired, as with exposure to carbon monoxide; instead, animal experiments and experience of humans indicate that hypersusceptibility may result from exposure to the gas.

Original from THE OHIO STATE UNIVERSITY

The toxic effects produced by hydrogen sulfide vary considerably with the concentration and also to some extent with individaul susceptibility. In low concentration, it has an irritant action on the air passages somewhat similar to but less intense than that of chlorine. In high concentration, hydrogen sulfide has a systemic effect, and in acute poisoning death is as rapid as in poisoning by cyanide (8).

Even in low concentrations, hydrogen sulfide exerts a marked irritant action upon the cornea of the eye. In experiments by the Bureau of Mines in connection with its investigation of toxic gases from Mexican and other high-sulfur petroleums and products (2), 0.01 percent hydrogen sulfide was definitely irritating to human subjects, the lowest concentration to which they were exposed. With canaries and animals symptoms were observed in concentrations as low as 0.005 percent, and acute symptoms appeared in 0.02 percent. The data obtained for men disclose that their reaction to hydrogen sulfide is similar to that of animals.

A survey of the petroleum operations suspected of having a hydrogen sulfide hazard in the investigation mentioned above revealed that many of the cases of asphyxia occurred at the storage tanks. With but few exceptions, all of the storage tanks investigated contained highly toxic concentrations of hydrogen sulfide. For instance, samples of light Mexican crude taken in storage tanks at 4 inches to 4 feet above the oil contained concentrations of hydrogen sulfide varying from 0.03 to 0.56 percent. Men have been found dead on the open derrick floor, presumably caught by the first burst of gas when they "drilled-in." During early experience with large quantities of hydrogen sulfide gas, when operations were conducted without respiratory protection, as many as 31 cases of unconsciousness were reported in closing-in one well; in similar operations, men have fallen into derrick cellars and sustained additional injury. Connection men have been overcome in ditches, and gagers have sometimes been overcome so suddenly that they have fallen off storage tanks. Persons have been fatally gassed by walking into ditches, ravines, and depressions in which the gas had accumulated. The common occurrence of dead rabbits and birds around storage tanks, especially inside the fire walls, is evidence of the danger. An experience has been cited (9) in which a man lost consciousness while driving a car through a tank farm; the car passed out of the path of the gas before coming to a stop and the man regained consciousness.

In another instance (9), a sudden shift of the wind caused all the mules in a corral to be killed by the gas as it moved in their direction. Men have been killed on entering tankship compartments and storage tanks for the purpose of cleaning or repairing. At refineries, fatal cases of poisoning have occurred at a wide variety of places. Men have been overcome while walking along a battery of batch stills; while repairing empty condenser cooling-water tanks in which sewer connections were not closed; in pressure-still houses while attempting to close leaky valves; in pipe-line ditches; and while gaging and cleaning tanks (2).

In its study of hydrogen sulfide poisoning in the Texas Panhandle and the Big Lake and McCamey, Texas, oil fields (10), the Bureau found that the hydrogen sulfide content of the gas in the McCamey field averaged about 5 percent. The minimum proportion of this gas in a mixture with air that will cause immediate unconsciousness is 1 part to about 50 parts of air. A mixture of 1 part of the Big Lake gas (which contained about 10 percent hydrogen sulfide) with 100 parts of air was highly toxic. Recent investigations by the Bureau of Mines (11) in the Elk Basin area of Wyoming indicated a dangerous hazard to life from the gas in the oil of the Tensleep formation, which has a hydrogen sulfide content of 18 percent. Another field investigated by the Bureau (12) in which there is a possible hydrogen sulfide hazard is the Magnolia oil field in Arkansas, where the gas produced with the oil has a hydrogen sulfide content of 2.22 percent by volume. The hydrogen sulfide content of the gas produced in other fields also has been reported by the Bureau (13).

Following is a summary (8) of the physiological response to various concentrations of hydrogen sulfide:

Period of exposure	Parts of hydrogen sulfide per million parts of air
Maximum allowable concentration for prolonged exposure ..	20
Slight symptoms after exposure of several hours	70-150
Maximum concentration that can be inhaled for 1 hour without serious consequences	170-300
Dangerous after exposure of 30 minutes to 1 hour	400-700
Fatal in exposure of 30 minutes	600

The maximum permissible concentrations of hydrogen sulfide in air accepted and published by the American Standards Association is 20 parts per million by volume, corresponding to 0.028 milligram per liter of air at 25° C. and 760 mm. Hg. for exposure not to exceed a total of 8 hours daily (14).

PHYSIOLOGICAL ACTION OF HYDROGEN SULFIDE

Two distinct types of accidents are caused by gas from high-sulfur crudes - asphyxia and irritation. The poisoning produced by different concentrations of hydrogen sulfide may be divided into acute, resulting in almost instantaneous asphyxia with seeming respiratory paralysis, and subacute, resulting in irritation, principally of the eyes and respiratory passages, followed by depression of the central nervous system. A concentration of hydrogen sulfide a few hundredths of 1 percent higher than that causing irritation can asphyxiate. Preliminary studies by the Bureau (2) of the toxicity of hydrogen sulfide indicated that men could not safely be used as experimental subjects because of possible serious injury to the lungs and the narrow margin between consciousness and unconsciousness and between unconsciousness and death. Some men were exposed for short periods to hydrogen sulfide in low concentrations, however, and the results obtained, considered with those reported by others, gave enough data to predict the reaction of men to higher concentrations.

Death in acute hydrogen sulfide poisoning results from failure of respiration and consequent asphyxia. This respiratory failure is occasioned through two separate processes, depending on the concentration of the gas inhaled. Moderately high concentrations may cause abnormal exaggeration of the respiratory movements by stimulating the respiratory center. Excessive breathing lowers the carbon dioxide content of the blood, which causes a temporary decrease or even cessation of respiration. Very high concentrations cause respiratory paralysis. Spontaneous breathing does not return after the paralytic form of failure unless artificial respiration is applied. After the overstimulation form of failure, breathing may return spontaneously.

In less severe poisoning, convulsions and shortness of breath are marked symptoms. In subacute poisoning the minimum symptoms are those of irritation, particularly of the eyes, and to a less degree of the respiratory tract (2). Observations by the Bureau show that eye and respiratory-tract irritations is prevalent among the men in the petroleum industry exposed to gas containing hydrogen sulfide. The eye irritation ranges in severity from mild conjunctivitis to swelling and bulging of the conjunctiva, photophobia (abnormal intolerance of light), and temporary blindness. In many cases these symptoms are extremely painful and cause much loss of time. In some instances, drilling has had to be suspended owing to the affection of the entire crew.

There are many cases of respiratory irritation, but they are not as numerous as the conjunctivitis cases. Irritation of the nose, throat, and lungs often leads to rhinitis, laryngitis, and bronchitis (2). Irritation of the respiratory tract may be followed by edema of the lungs (2). Although direct irritation of the lungs or coughing may cease with removal from exposure to the gas, there is still danger of pneumonia or fluid in the lungs later. Chronic hydrogen sulfide poisoning from constant exposure may result in mental depression, weakness, sweats, and frequent chills.

TREATMENT OF HYDROGEN SULFIDE POISONING

As hydrogen sulfide in the blood oxidizes rapidly, symptoms of acute poisoning pass off when inhalation of the gas ceases. It is imporatant, therefore, to get the victim of poisoning to fresh air as quickly as possible. He should be kept at rest and chilling should be prevented. If respiration is slow, labored, or impaired, artificial respiration may be necessary. This, however, should be performed with great caution owing to congestion of the lungs (14). Artificial respiration should be supplemented by administration of oxygen or a mixture of oxygen and carbon dioxide. Every man working around crude oil containing hydrogen sulfide should be able to give artificial respiration by the Schaefer prone-pressure method, as most persons overcome by hydrogen sulfide gas may be revived if artificial respiration is applied before the heart action ceases. In acute poisoning, the persistent administration of oxygen is of great value (15). Victims of poisoning should be under the care of a physician. Irritation due to subacute poisoning may lead to serious results, such as pneumonia. Under those conditions, treatment by the physician necessarily would be symptomatic. The patient should be kept in fresh air and hygienic conditions should be watched carefully.

Treatment of conjunctivitis consists of irrigation with boric acid solution, followed by argyrol, usually 10 percent. In more pronounced cases, a bland ointment, such as vaseline, neutral petrolatum, or boric acid ointment, should be applied to the lids. In severe cases, when pain is marked, ice compresses are beneficial, applied for 15 minutes to an hour three times a day. Instillation of 3 drops of a 1-percent solution of holocain every 3 hours for the first 24 hours, then at longer intervals, will give temporary relief. The use of atropine, 1 drop of 1 percent every 4 hours, may be necessary to dilate the pupil if inflammation is likely to extened from the cornea to the iris. The treatment for the eyes recommended in this paragraph should be administered under the direction of a physician. The patient should remain indoors and in the dark as far as possible. Early use of smoked glasses will relieve the strain on the eyes when the patient goes out of doors or when the light is bright. The prognosis (progress to recovery) in those cases usually is good.

Pharyngitis is indicated by dryness of the throat, usually with a dry cough. The patient may complain of pain and the sensation of a foreign body in the throat. Application of a solution of 10 percent of silver nitrate or argyrol is advisable; the use of an oily spray may aid. The prognosis is good.

Bronchitis is recognized by a feeling of tightness and rawness in the chest and a cough that is persistent but usually dry at first. The expectoration, which is scanty but tenacious at first, usually becomes abundant and mucopurulent (containing both mucus and pus). Temperature may accompany this condition, but usually the poisoning is not so severe, as the men realize they are breathing an irritating atmosphere and leave it as soon as possible. The prognosis is good if the men are not subjected to repeated exposures.

The use of an expectorant is advisable. Dover's powders, a mixture of squills, ammonia, and senega, or elixir terpine hydrate are excellent. The patient, if feverish, should be confined to bed (2). Men who develop pharyngitis or bronchitis from exposure to hydrogen sulfide should be under the care of a physician.

PREVENTION OF HYDROGEN SULFIDE POISONING

Precautions

Many cases of irritation are the result of carelessness, negligence, or lack of knowledge of the danger on the part of either the employee or the employer. Men often stand needlessly on the leeward side of the wellhead or in the stream line flow of the gas. Workmen should be instructed to avoid the gas whenever possible by working on the windward side of the outlet from which the gas is escaping. Under no condition should a man stand directly over a thief or gage hole on a tank. Three out of five reported deaths resulting from hydrogen sulfide gas in some of the fields investigated by the Bureau have occurred to gagers on top of tanks.

As in all safety work, education in avoiding the hydrogen sulfide hazard is attended with many difficulties, and an additional responsibility is placed upon foremen and superintendents in fields where this gas occurs. Instructive bulletins regarding the hazard and the necessity of keeping out of the gas as much as possible should be **issued,** and men in charged of work should show by their own example what precautions should be taken when in the gas.

Protective Equipment

Employers should furnish the following protective equipment and insist that men working in atmospheres containing hydrogen sulfide gas wear this equipment.

Men should be instructed in proper use of each type.

1. For work in cellars, inside of tanks or in other confined spaces where high concentrations of hydrogen sulfide gas may occur, men should wear hose masks equipped with blowers. Care should be taken that the blowers are far enough away from gas so that the men will be sure to have an uncontaminated supply of air. As an extra precaution, a man should be designated to watch each hose and safety line and to keep them from becoming tangled. Workmen should not enter these places without a safety belt and life line and someone always attending the life line to pull them to safety if necessary. A special oilproof hose should be specified for all petroleum industry use (16).

2. For work on the derrick floor, where concentrations of hydrogen sulfide are likely to occur that will irritate the eyes, men should wear a gas-tight type of goggle. Goggles with water dams, to overcome fogging of the lenses, and nonshattering glass are recommended.

3. For gaging tanks and other outside exposures, including the derrick floor, where low concentrations of hydrogen sulfide gas exist that irritate the respiratory tract, suitable canister-type masks should be worn.

Education in the limitations of the canister mask is essential. A canister mask is a filter, not a generator of oxygen, and is intended only for low concentrations of hydrogen sulfide.

For gaging tanks, there is the objection to the canister mask that the wearer may feel himself immune from all danger and stand in the streamline flow of a highly toxic gas escaping from an opened vent or gage hole.

Canisters should be used in accordance with the instructions of the manufacturers, as they know the contents of the container and the safe working time that is permissible before discarding it. The life of a canister is relatively short.

Original from THE OHIO STATE UNIVERSITY

DETECTION OF HYDROGEN SULFIDE IN AIR

The Bureau of Mines (17) has developed a hydrogen sulfide detector suitable for use where high-sulfur petroleum is being produced or refined. It is simple enough for the average laborer to obtain accurate results after reading a few directions. It gives rapid results and is accurate enough to indicate at least semiquantitatively concentrations in air ranging from those that are harmless, or but slightly harmful, to those immediately dangerous to life. The operation of the detector is based upon a color-change reaction on the surface of sensitized granules placed in a glass tube, through which the atmosphere to be examined is aspirated by means of a rubber bulb or hand pump. The amount of hydrogen sulfide is indicated either by the distance the color change travels in the column of granules for a constant sample volume or the volume of sample required to produced a standard length of travel. Granules of activated aluminum oxide (20 to 24 mesh) coated with silver cyanide or lead acetate are satisfactory for estimating hydrogen sulfide in the range of 0.0025 to 0.05 percent by volume in air. The function of the detector was examined at temperatures of minus 22° to plus 25° C. (minus 7.6° to plus 77° F.) and found to be satisfactory. Detector tubes filled with silver cyanide-coated granules retained their sensitivity and usefulness after 18 months' storage and aging in ordinary laboratory daylight.

The British (18) have adopted the lead acetate test for hydrogen sulfide as a sensitive qualitative test easily adapted to a quantitative basis. By this method, a known volume of the atmosphere is drawn into contact with a lead acetate paper on which glycerol is incorporated to keep it slightly moist. Strips of filter paper are immersed for 1 minute in a reagent prepared by dissolving 10 g. lead acetate (Reagent quality) in 90 ml. of distilled water and adding 5 ml. of glacial acetic acid and 10 ml. of pure glycerol to the solution. The superfluous liquid is allowed to drain off, and the papers are suspended vertically in an atmosphere free from hydrogen sulfide and allowed to dry as completely as possible at the ordinary temperature. When dry, 1 inch at the top and bottom of each strip is trimmed off and discarded, and test papers are stored in a glass-stoppered, air-tight container. Fresh test papers are prepared every fortnight.

The atmosphere is sampled and tested by a hand exhaust pump; the lead acetate paper is clamped in a holder of special design, which is screwed into the pump. Indication of the atmosphere is obtained by making slow and steady strokes of the pump, after which the paper is removed and compared within 10 minutes with a standard color chart. A positive test will be obtained if the concentration of hydrogen sulfide is greater than 1 part in 60,000 (0.025 mg. per liter).

A number of automatic devices (19) are available for recording continuously the quantity of hydrogen sulfide in air by impinging the air though a fine jet against a rotating drum, on which is a chart of lead acetate paper. One of these devices is so arranged that the stain produced by the hydrogen sulfide causes a change in the optical transparency of a strip of paper, which, in turn, interferes with a ray of light directed on a photoelectric cell and causes a bell to ring.

BIBLIOGRAPHY

1. Dublin, Louis I., and Vane, Robert J. Occupation Hazards and Diagnostic Signs. Div. of Labor Standards Bull. 41, 1941, p. 60.

2. Sayers, R. R., Smith, N. A. C., Fieldner, A. C., Mitchell, C. W., Jones, G. W., Yant, W. P., Stark, D. D., Katz, S. H., Bloomfield, J. J., and Jacobs, W. A. Investigation of Toxic Gases From Mexican and Other High-Sulfur Petroleum Products. Bureau of Mines Bull. 231, 1925, 108 pp.

3. Journal Chemical, Metallurgical and Mining Society of South Africa. The Effect of Humidity on the Toxicity of Hydrogen Sulphide Gas. Vol. 36, 1936, pp. 378-384.

4. Oil and Gas Journal. Hydrogen Sulfide Reacts on the Nervous System. Vol. 42, 1944, pp. 50-51.

5. Gregory, Thomas C., editor. The Condensed Chemical Dictionary. 3d. ed. 1942, 756 pp.

6. Coward, H. F., and Jones, T. W. Limits of Inflammability of Gases and Vapors. Bureau of Mines Bull. 279 (revised). 1939, 146 pp.

7. **Science** and Art of Mining. Mine Gases and Gas Testing: Hydrogen Sulfide and Nitrous Oxide. Vol. 533, 1942, p. 112.

8. Henderson, Yandell, and Haggard, Howard W. Noxious Gases and the Principles of Respiration Influencing Their Action. 1943, 294 pp.

9. Aves, C. M. Hydrogen Sulphide Poisoning in Texas. Texas State Jour. Med., vol. 24, 1929, p. 761 (Ab. Jour. Indust. Hyg., vol. 11, 1929, pp. 240-242.)

10. Yant, W. P., and Fowler, H. C. Hydrogen Sulfide Poisoning in the Texas Panhandle, Big Lake, Texas, and McCamey, Texas, Oilfields. Bureau of Mines Rept. of Investigations 2776, 1926, 20 pp.

11. East, J. H., and Espach, Ralph, H. Occurrence of Hydrogen Sulfide Gas in the Elk Basin Oil Field of Wyoming. Bureau of Mines Information Circular 7334, 1945.

12. Carpenter, Charles B., and Schroeder, H. J. Magnolia Oil Field, Columbia County, Ark. Part I. Petroleum Engineering Study. Bureau of Mines Rept. of Investigations 3720, 1943, pp. 1-74.

13. Devine, J. M., and Wilhelm, C. J. Hydrogen Sulfide Content of the Gas in Some Producing Fields. Bureau of Mines Rept. of Investigations 3128, 1931, 15 pp.

14. Division of Industrial Hygiene. Hydrogen Sulfide: Its Toxicity and Potential Dangers. National Institute of Health. Reprint 2256 from Public Health Reports. Vol. 56, 1941, pp. 684-692.

15. Journal of the Chemical, Metallurgical and Mining Society of South Africa. Hydrogen Sulfide Poisoning. Vol. 37, 1936, p. 95.

16. Fowler, H. C. Prevention of Hydrogen Sulfide Poisoning in Handling and Refining High-Sulfur Petroleums. Bureau of Mines Rept. of Investigations 2847, 1927, 26 pp.

17. Littlefield, J. B., Yant, W. P., and Berger, L. B. A Detector for Quantitative Estimation of Low Concentrations of Hydrogen Sulphide. Bureau of Mines Rept. of Investigations 3276, 1935, 13 pp.

18. Department of Scientific and Industrial Research. Methods for the Detection of Toxic Gases in Industry. Leaflet No. 1. Hydrogen Sulfide. His Majesty's Stationery Office, London, 1943, 5 pp.

19. Jacobs, Morris B. The Analytical Chemistry of Industrial Poisons, Hazards and Solvents, New York, 1941, pp. 252-259.